Project report on

PREPARATION AND CHARACTERIZATION OF COPPER-CHROMIUM NANOSTRUCTURES BY MECHANICAL MILLING

Submitted by

Ankur Sharma

and

Nishank Kanungo

Under the guidance of

Dr. Suhrit Mula

Department of Metallurgical and Materials Engineering

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Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**Preparation and characterization of copper-chromium nanostructures developed by mechanical milling**" submitted by **NISHANK KANUNGO (10604013) and ANKUR SHARMA (10604021)** in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

Dr. Suhrit Mula, Assistant Professor
Dept. of Metallurgical and Materials Engg.
National Institute of Technology Rourkela-769008

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Abstract

Synthesis and characterization of $Cu_{96}Cr_4$ and $Cu_{95}Cr_5$ nanostructures developed by high energy ball milling have been carried out in the present study. Mixtures of Copper and Chromium in the desired quantities were ball milled in stainless steel grinding media to prepare the required nanocomposites. Toluene was used as process control agent. Mill speed was maintained at 400 rpm and milling was continued for 50 h. The extents of alloying, structural and morphological changes of the nanocomposites in the powder form were analyzed and studied using X-ray diffractometer, Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (EADX). X-ray diffraction data was analyzed by using X'Pert highscore plus for the determination of crystallite size and lattice microstrain (%). The powder samples were then compacted under uniaxial pressing using a pressure of 690MPa. The pellets were then sintered in nitrogen atmosphere at 900°C for a soaking period of one hour. The sintered specimens were again studied using SEM and XRD for microstructural analysis. The Vickers microhardness of the sintered samples was also measured.

Keywords: Nanostructure; Nitrogen atmosphere; Uniaxial pressing; Microstructure; Microhardness; Scanning electron microscopy (SEM); X-ray diffraction (XRD); Energy dispersive X-ray spectroscopy (EDAX).

1. Introduction

Because of high electrical and thermal conductivity, copper and its alloys have found widespread applications, such as resistance welding electrodes, high voltage switches, motor commutators, continuous casting moulds and others [1]. Besides high mechanical properties and high electric and thermal conductivity it is increasingly more often required that properties of the copper alloys remain stable in different operating conditions, and often also that they are resistant to varying force, current and thermal loads. Some compromise in this regard can be achieved using precipitation hardened alloys, which have to be sometimes subjected to the additional thermo-mechanical treatment [2-6]. The major problem with these materials is instability of their mechanical properties and electric and thermal conductivity at elevated temperatures, resulting from temperature instability of their microstructure. These materials with conventional grain size are soft materials with relatively low yield strength and very low wear resistance. Conventional Cu-based composites can improve the required strength but conductivity decreases to an unacceptable range. The properties of Cu based composites might be increased by nanosize reinforcement than micro size [7, 8]. The performance of these materials is expected to be enhanced if the nanosize grain is retained in bulk material with nanosize distribution of second phase particle. This can provide unique characteristics, such as high thermal and electrical conductivities, as well as, high mechanical strength and excellent resistance to high temperature annealing [9].

Due to these basic problems associated with copper and its alloys a lot of work in the past few years has gone into the development of copper based nanocomposite which has gone a long way in eliminating the drawbacks of copper based materials. A lot of effort in this regard has gone to the development of copper based nanocomposites by mechanical milling and characterization of these nanocomposites by using SEM, Transmission Electron Microscope (TEM) and XRD techniques. The proposed works aims to study the development and characterization of copper-chromium nanostructures.

2. Aim and Objective

The present work aims at:

- Preparation of Copper – Chromium nanocomposites with varying amounts of chromium.
- Characterization of the prepared powder by using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDAX) study.
- Compaction of the powdered sample by using uniaxial hydraulic press at a desired pressure.
- Sintering of the prepared pellets in a controlled atmosphere at a pre-decided temperature.
- Characterization of the sintered nanocomposites by using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD).
- Hardness testing of the sintered specimen using Vickers microhardness.
- Analysis of the results and establishment of suitable mixture ratio for the best properties.

3. Plan of work:

1. Literature review.
    a. Nanocomposite
    b. Mechanical milling
    c. Conversion of atomic percent to weight percent and vice versa
    d. Effect of ball milling on copper nanocomposite
    e. Effect of milling time on Cu-NbC nanocomposite

2. Experimental
    a. Preparation of copper – Chromium nanocomposites by ball milling
    b. SEM, EDAX and XRD study of prepared powder nanocomposite.
    c. Compaction and sintering of powder nanocomposite.
    d. SEM and XRD study of prepared sintered nanocomposite.
    e. Hardness testing of sintered specimen.

3. Analysis of Data.
4. Result and Conclusion.

1. Literature review.

Nanocomposite

A nanocomposite can be defined as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material [10]. In a way this definition can include porous media, colloids, gels, but is generally considered to be the solid combination of a bulk matrix and nano-dimensional phase(s) which differ in their various properties due to dissimilarities in structure and chemistry [11]. The various properties of the nanocomposite will markedly different from that of the component materials. Size limits for these effects have been proposed, <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving super-paragmatism mechanical strengthening or restricting matrix dislocation movement [12].

According to mechanical terms, nanocomposites are different from conventional composite materials due to the very high surface to volume ratio of the reinforcing phase and/or because of its very high aspect ratio. The reinforcing material can be made up of fibers, sheets or particles. The interfacial area between the matrix and reinforcement phase(s) is generally an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement.

This high surface area contributed by the reinforcement phase means that the macroscale properties of the composite will vary largely due to a relatively small amount of nanoscale reinforcement. For example, adding carbon improves the electrical and thermal conductivity. Other kinds of nanoparticulates may result in enhanced optical properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage. In general, the nano reinforcement is dispersed into the matrix during processing. The *mass fraction* of the nano-particles introduced is very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most

commonly used non-spherical, high aspect ratio fillers like nanometer-thin platelets, or nanometer-diameter cylinders.

Mechanical Milling

Mechanical Milling is generally carried out using a ball mill. A ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis and the drums of the ball mill are partially filled with the material to be ground plus the grinding medium. Different materials that are used as media include ceramic balls, flint pebbles and stainless steel balls. An internal cascading effect reduces the material to a fine powder.[13] Industrial ball mills generally operate continuously, by taking the fed at one end and discharging at the other end. Large to medium-sized ball mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion). High-quality ball mills are potentially expensive and can grind mixture particles to as small as 5 nm, enormously increasing surface area and reaction rates. The grinding works on principle of critical speed. The critical speed can be understood as that speed after which the steel balls (which are responsible for the grinding of particles) start rotating along the direction of the cylindrical device; thus causing no further grinding.

Ball mills are used extensively in the Mechanical alloying process[14] in which they are not only used for grinding but for cold welding as well, with the purpose of producing alloys from powders.

There are many types of grinding media suitable for use in a ball mill, each material having its own specific properties and advantages. Common in some applications are stainless steels balls. While usually very effective due to their high density and low contamination of the material being processed, stainless steel balls are unsuitable for some applications, including:

- Black powder and other flammable materials require non-sparking lead ,antimony, brass , or bronze grinding media
- Contamination by iron of sensitive substances such as ceramic raw materials. In this application ceramic or flint grinding media is used. Ceramic media are also very resistant to corrosive materials.

High density alumina media (90–95% alumina) is widely used in the ceramic industry to grind clay bodies, frits, glazes and other ingredients. It is more expensive than silica / silex media but is more efficient [15].

Ball Milling of Cu-Nanocomposite

The ball milled materials were obtained as small solid spheres of up to 8mm diameter through in situ consolidation during milling [16].

The miniaturized tensile tests of the nanocrystal materials clearly demonstrate high strength along with good ductility. The ball milled nanocrystal Cu exhibits ultra high strength and large ductility compared to other nanocrystal materials produced so far.

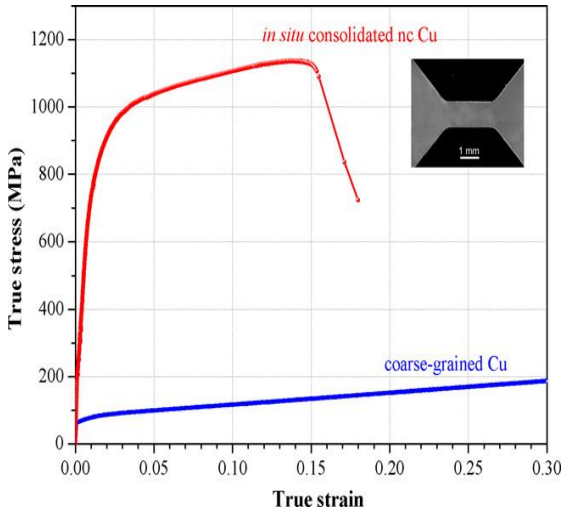

Fig. 4.1: True Stress vs. true strain for nanocrystal Cu and coarse grained Cu (Ref.17).

The high strength in the elemental nanocrystal materials is due to the refined grain size effect. The exact reason for the large amount of ductility in the in situ consolidated ball

milled nanocrystal materials is not yet known; it could possibly be attributed to the lack of processing artifacts in the materials [18]

Ball milled nanocrystal Cu shows continuous strain hardening. In situ deformation studies conducted in TEM at OakRidge National Labs, Tennessee, USA, on artifact free ball milled nanocrystal Cu showed dislocation pile ups even in smaller grains (~25 nm) and the authors believe that the presence of dislocation activity is responsible for the observed strain hardening.

The tensile curves for enc Cu show a rapid strain hardening in the early stages of plastic deformation followed by wide flat region with little strain hardening behavior in the later stages. This is consistent with most of the literature reported on nanocrystal and ultrafine grain (UFG) Cu. In most of the cases the strain hardening behavior was observed only at low plastic strains with an exception of electrodeposited Co which showed strain hardening up to 6% plastic strain. According to Ma et al., the faster strain hardening rate in the early stages in nanocrystal materials with few larger grains could be a result of dislocation activity in larger grains. The larger grains saturate after a certain extent of plastic deformation while little dislocation activity is anticipated in smaller grains. Thus, the decreased dislocation activity with increasing plastic strain results in flattening of the tensile curves in the later stages. Such an approximately elastic–perfectly plastic nature is completely different from the continuous strain hardening observed in cgs metals. This mechanism is contrary to the strain hardening behavior observed in the present ball milled nanocrystal Cu. The exact reason for such differences is not clear at the present time [19].

Effect of milling time

Most of the investigations of *in situ* mechanically alloyed copper-based composite such as Cu–NbC have mostly focused on the synthesizing process of the powder. Little

information is available regarding the effects of milling parameter on physical and mechanical properties of the *in situ* copper-based composite. The relationship among microstructure, phase formation and properties has yet to be fully understood.

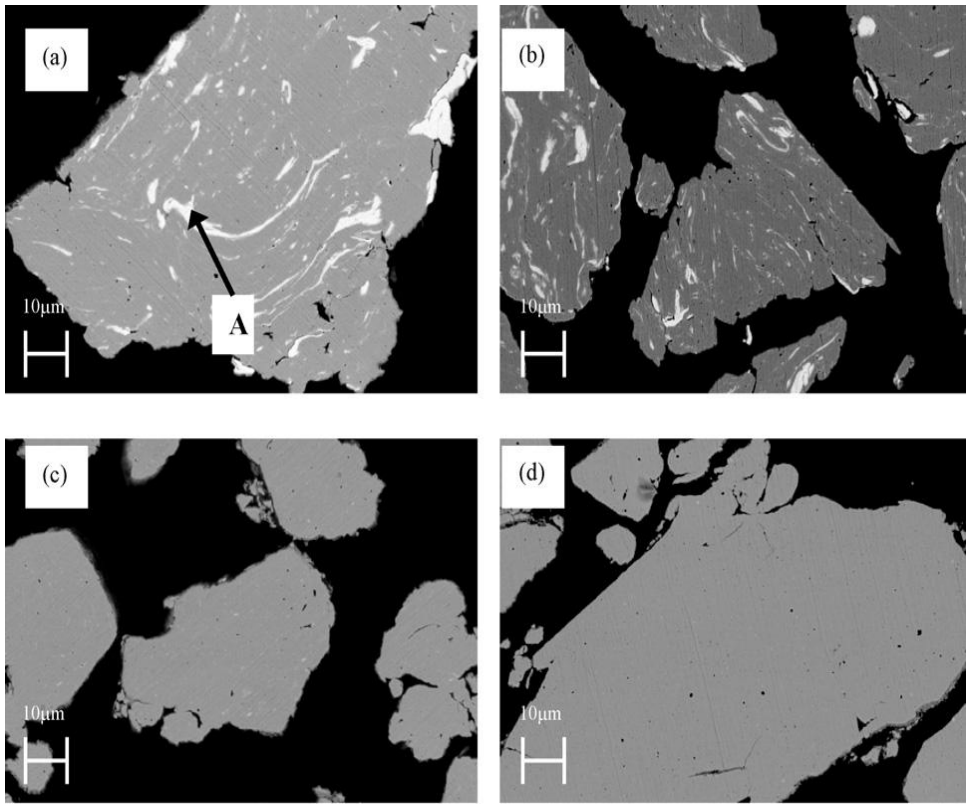

Fig 4.2: Variation in the microstructure of Cu-NbC nanocomposites with varying time of mechanical alloying. (Ref. 20)

The results of this study showed that NbC phase appears in Cu–Nb–C pellet, which had been prepared by mechanical alloying and subsequent sintering. The crystallite size of Cu and NbC decreased while the internal strain increased with the increase of milling time. The *in situ* composite exhibited higher microhardness because of the refinement of the NbC particle [21].

Conversion of atomic percent to weight percent and vice versa.

A) Converting from atomic percent to weight percent:

1. For each element listed in the compound, multiply the atomic percent of the element by its atomic weight [the larger of the two principal numbers listed for each element in the standard periodic table]. For each element, let's call this value ***p***.
2. Add all the values of ***p*** together, and let's call this value ***p(Total)***.
3. Now, for each value of ***p***, divide it by ***p (Total)***, to obtain ***w***.
4. Multiplying the resulting values of ***w*** by 100 gives us the weight percent values, for each respective element in the starting compound.

B) Converting from weight percent to atomic percent:

1. For each element listed in the compound, divide the weight percent of the element by its atomic weight. For each element, let's call this value ***m***.
2. Add all the values of ***m*** together, and let's call this value ***m (Total)***.
3. Now, for each value of ***m***, divide it by ***m (Total)***, to obtain ***a***.
4. Multiplying the resulting values of ***a*** by 100 gives us the atomic percent values, for each respective element in the starting compound.

5. Experimental work done.

Materials used:

1. $Cu_{96}Cr_4$ (in atomic percentage).
2. $Cu_{95}Cr_5$.

High energy ball Mill

Milling was done in planetary ball mill (FRITSCH Pulverisette 5). Stainless steel balls were used as the milling media and the ball mill was rotated at 400 rpm.
The ball to powder ratio used for milling was 10: 1. Toluene was used as the milling media as wet milling was done.
Powder sample was collected each after 2 h, 5h, 10h, 20h, 35h and 50h of milling for analysis.

X-ray Diffraction:

X-ray diffraction of the milled samples as well as sintered specimens was carried out in a Philips X-pert PRO high-resolution X-ray diffractometer. The phase evolution at different stages of milling was studied by using Cu-K_α (λ=1.54059**Å**) radiation. The data was analyzed for phases present, crystallite size and lattice micro strain.

SEM Characterization:

Microstructural characterization of the milled powder and sintered compacts was carried out by using JEOL JSM-6480 LV scanning electron microscope. The microstructral refinement of the powder samples and surface morphology of the sintered specimen were investigated at different magnifications, for example, 500X and 1000X.

The images obtained from the SEM can give an idea of the micro structural changes in the nanocomposite with varying milling times. SEM images were taken for specimen 1 at two different magnifications and two different locations on the slide for each magnification. The accelerating voltage used in each case was 20 kV. EDAX was also carried out to check for compositional changes in the nanocomposites at different milling times.

Consolidation and sintering:

Powder nanocomposites have no use except in few cases like coating industry. To make it use for structural applications, powder particles are required to be consolidated into a bulk form.

For experimental purposes the prepared Copper-chromium nanocomposite was converted into pellets by using a die having 12mm diameter and a hydraulic press was used to apply a pressure of 8tonnes. Four pellets of varying thickness were made of each composition.
Sintering is a method for making objects from powder, by heating the material in a sintering furnace below its melting point (solid state sintering) until its particles adhere to each other. Most, if not all, metals can be sintered. This applies especially to pure metals produced in vacuum which suffer no surface contamination. Sintering under atmospheric pressure requires the usage of a protective gas, quite often endo gas. Sintering, with subsequent reworking, can produce a great range of material properties. Changes in density, alloying, or heat treatments can alter the physical characteristics of various products. For instance, the Young's Modulus En of sintered iron powders remains insensitive to sintering time, alloying, or particle size in the original powder, but depends upon the density of the final product.

The pellets were then sintered at a constant temperature of 900°C in nitrogen atmosphere for 1 h.

Microhardness measurement:

Microhardness testing of the sintered sample is done using Vickers micro hardness testing machine (Leco LV 700 Vickers hardness tester) using a load of 3Kgf. Five observations were for each specimen and the average value was calculated.

6. Results and Discussion:

X-ray diffraction:

The identity and phase evolution at different stages of mechanical alloying (MA) were studied by XRD analysis using the Cu Kα (λ=1.54059Å) in a Philip's X-pert PRO high-resolution X-ray diffractometer. Figure 6.1 and 6.2 show the modulation of the XRD patterns of $Cu_{96}Cr_4$ and $Cu_{95}Cr_5$ compositions with the progress of milling up to 50 h. It is interesting to note that Cu and Cr peaks are clearly visible after 50 h of milling. It is to be noted that the peak intensity gradually decreased and broaden with progress of milling in both cases. But, in case $Cu_{95}Cr_5$ broadening is more and decrease in the intensity is also higher. In both the cases, peaks related to $Cr_{23}C_6$ are also visible.

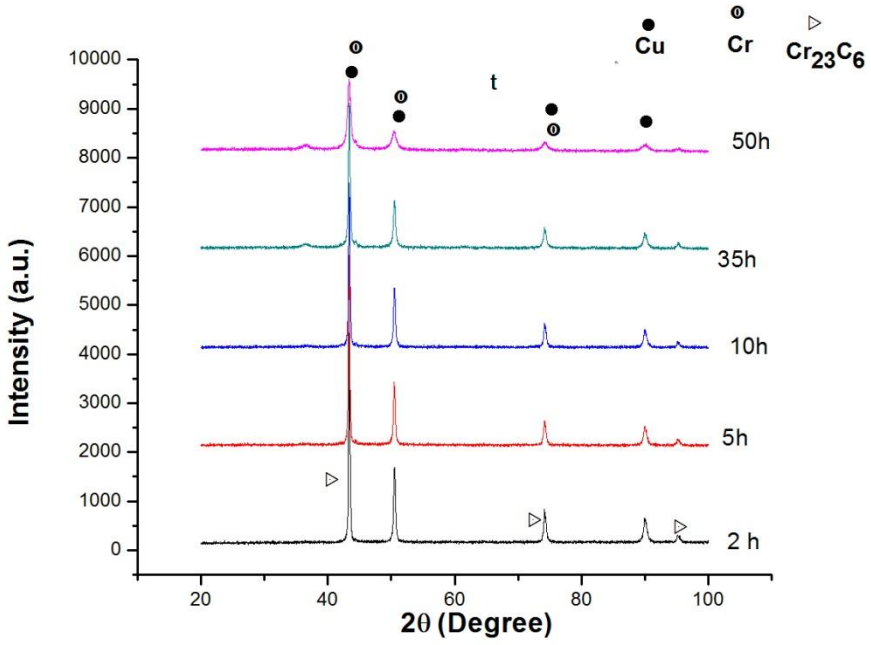

Figure 6.1

The fig. shows the phases present in a sample of composition 1 after varying times of ball milling along with their relative intensities.

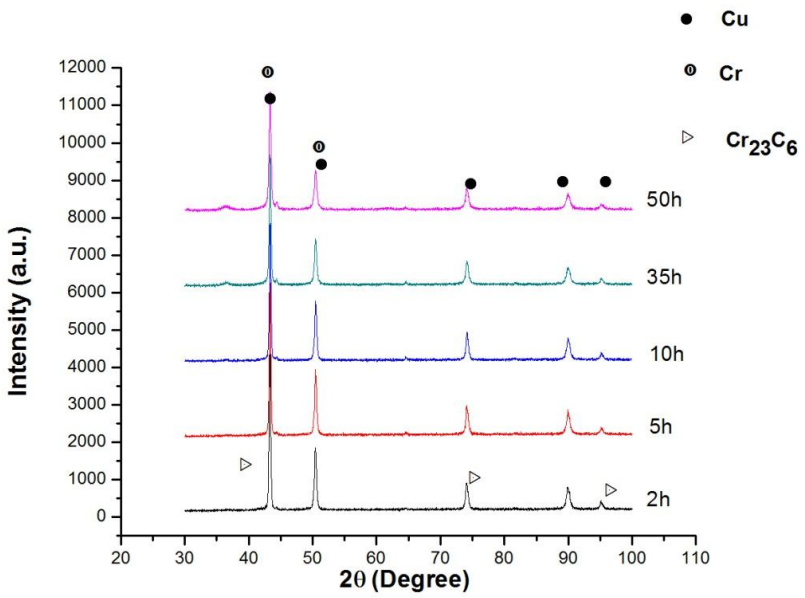

Figure 6.2

The fig. shows the phases present in a sample of composition 2 after varying times of ball milling along with their relative intensities.

Crystallite size vs. Milling Time.

With increase in milling time the crystallite size initially decreases rapidly then on further increase in milling time it has been found that the rate of decrease in crystallite size decreases and almost became constant. The increase in lattice microstrain (%) is also very rapid initially and then reaches nearly constant value, because of the plastic deformation and mechanical deforamtion.

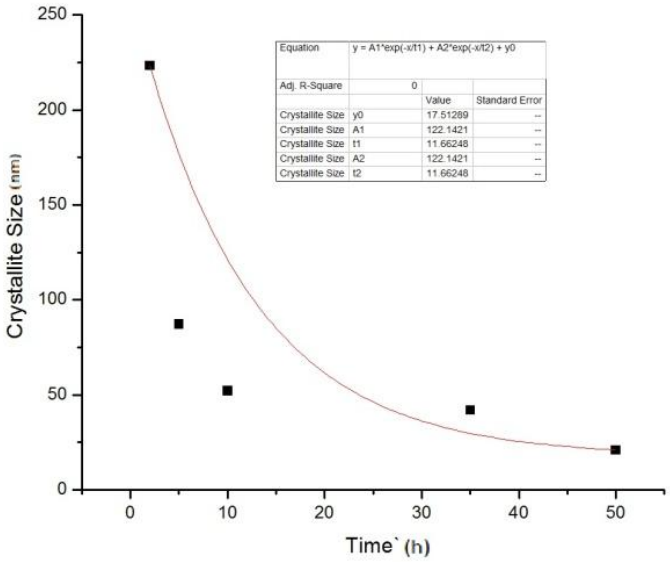

Figure 6.3

The graph shows that for composition 1 the crystallite size decreases with increase in milling time.

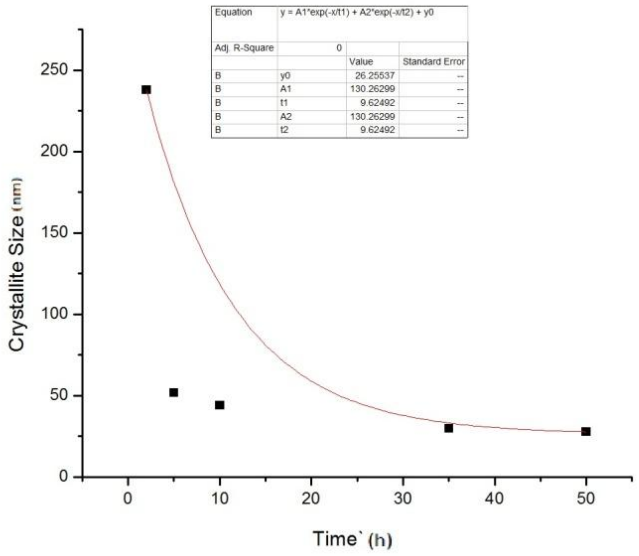

Figure 6.4

The graph shows that for composition 2 the crystallite size decreases with increase in milling time.

Lattice Strain vs. Time:

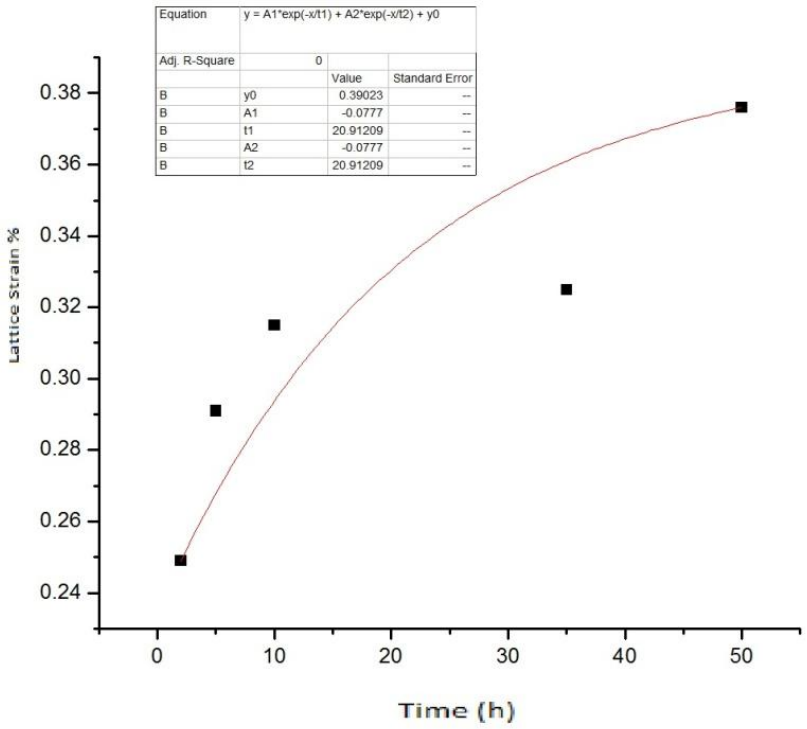

Figure 6.5

The figure shows that the lattice microstrain (%) increases with increase in milling time in case of composition 1.

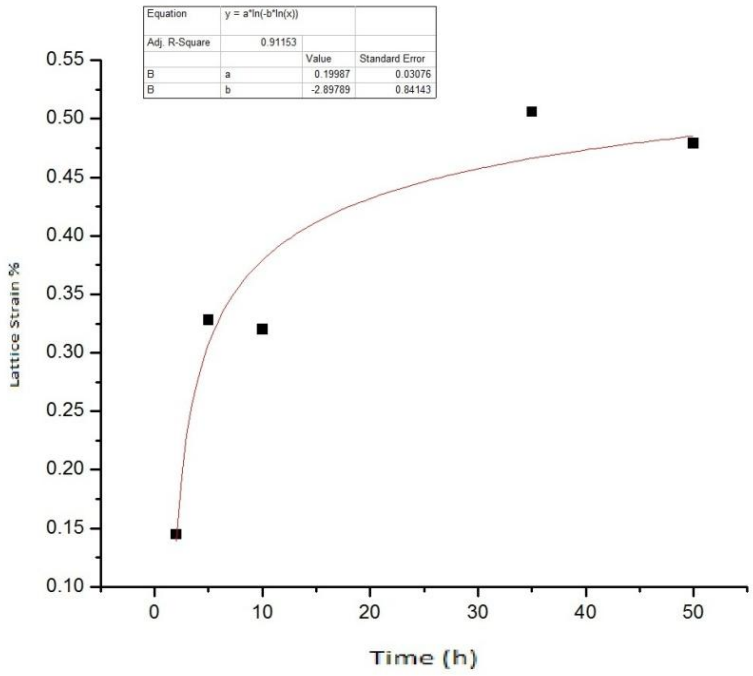

Figure 6.6

The figure shows that the lattice microstrain (%) increases with increase in milling time in case of composition 2.

SEM:

The images obtained from the SEM can give an idea of the micro structural changes in the nanocomposite with varying milling times. SEM images were taken for specimen 1 at two different magnifications and two different locations on the slide for each magnification. The accelerating voltage used in each case was 20Kv.

There is a definite decrease in the size of the nanostructures produced with increasing time of milling. When milling is started the powder material first start to agglomerate and

hence at two hours the size of the structures observed is very large. With increase in milling time the size of the structure starts to decrease successively.

Milling Time: 2h:

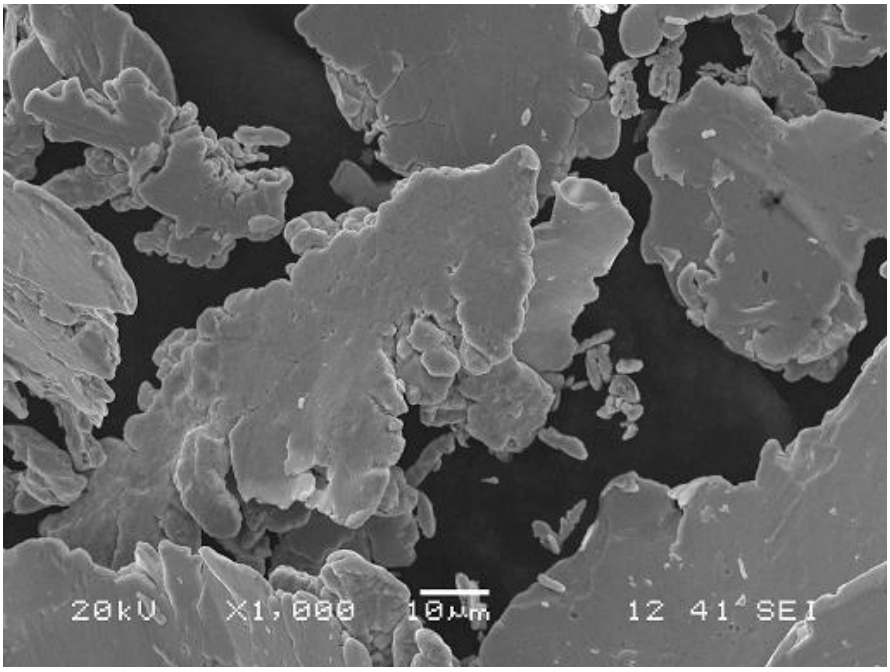

Figure 6.7

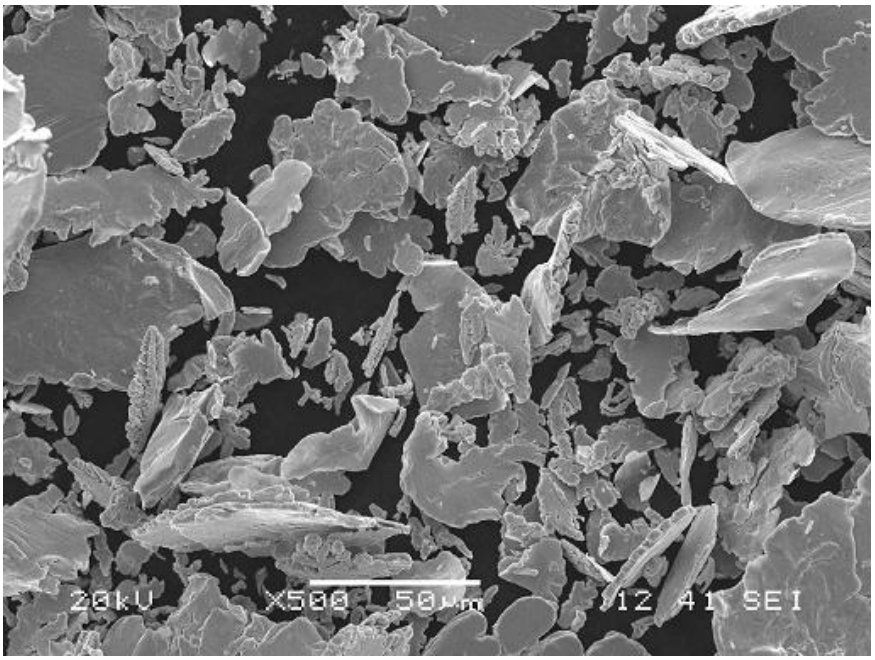

Figure 6.8

Images at magnification 1000X(Fig. 6.7) and 500X(Fig. 6.8). In Cu-Cr nanocomposite at low milling time the materials agglomerate as a result of which large chunks of materials can be seen in the SEM images.

Milling Time 10 h:

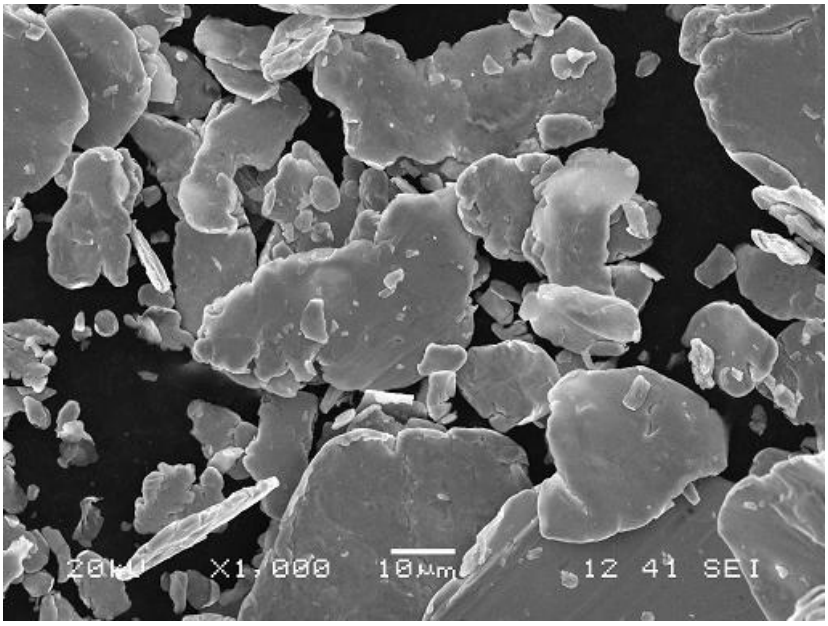

Figure 6.9

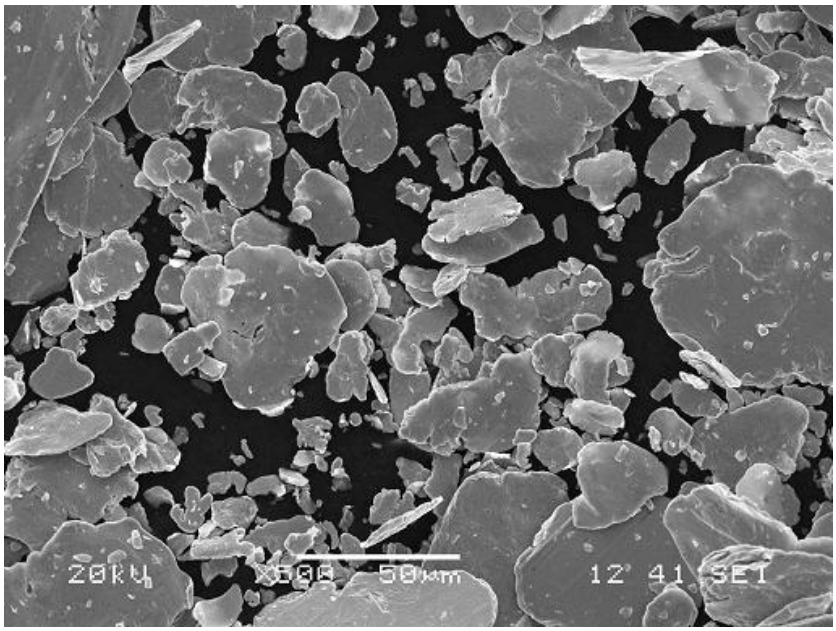

Figure 6.10

Images at magnification 1000X (Fig. 6.9) and 500X (Fig.6.10). With increase in milling time as can be seen there is a definite decrease in the size of the chunks as the agglomerated masses start to break of. Although larger sized chunks are still visible but the appearance of many smaller chunks definitely asserts the above fact.

Milling Time: 50 h

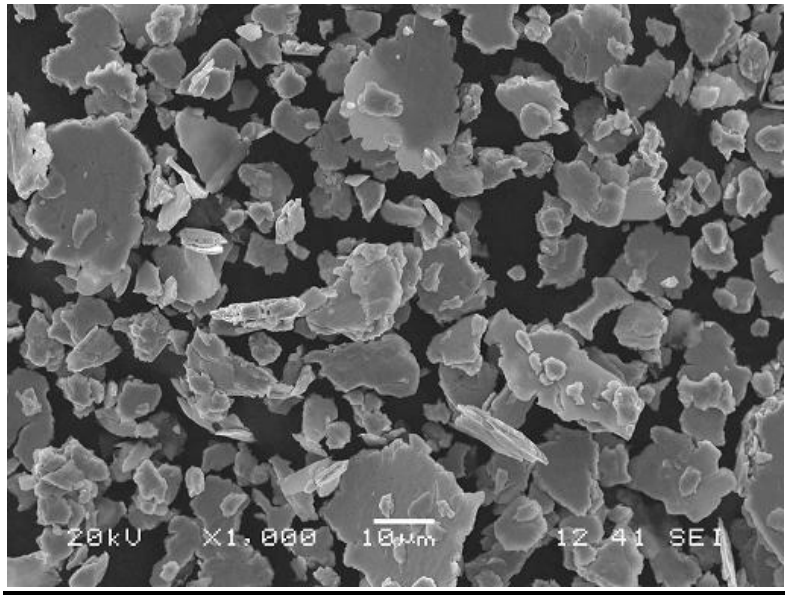

Figure 6.11

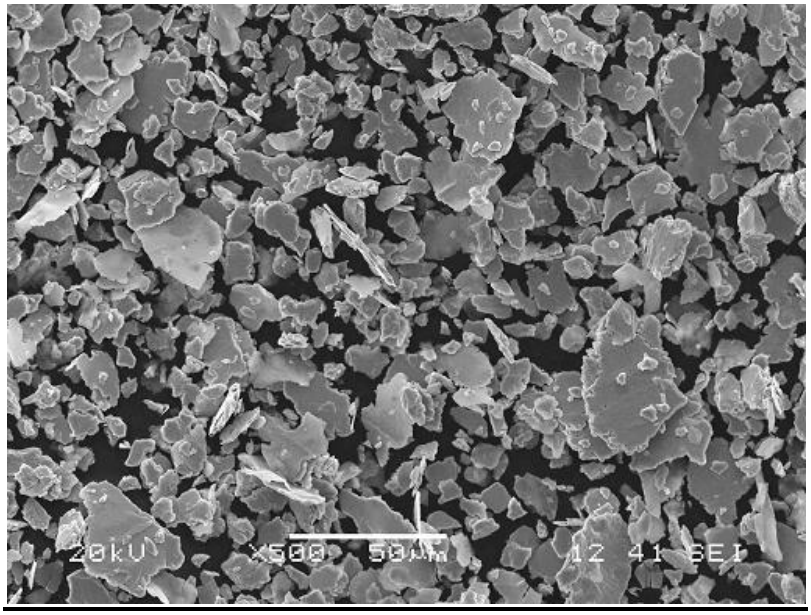

Figure 6.12

Images at magnification 1000X (Fig. 6.11) and 500X (Fig. 6.12). As can be clearly seen there is a drastic decrease in size of the particles with increased milling time. The agglomerated mass starts to break leading to smaller sizes.

Results from EDAX Analysis:

Initial composition of mixture used: $Cu_{96}Cr_4$ in atomic percentage. Cu = 99.09 (almost equal to 99) and Cr = 1 in weight percentage.

The specimen were subjected to EDAX analysis after milling them for 2H, 10 H and 50H. The results obtained have been shown below in both tabular and graphical forms.

Milling time: 2 h

Element	Atomic%
Cr K	0.22
Cu K	99.78
Totals	

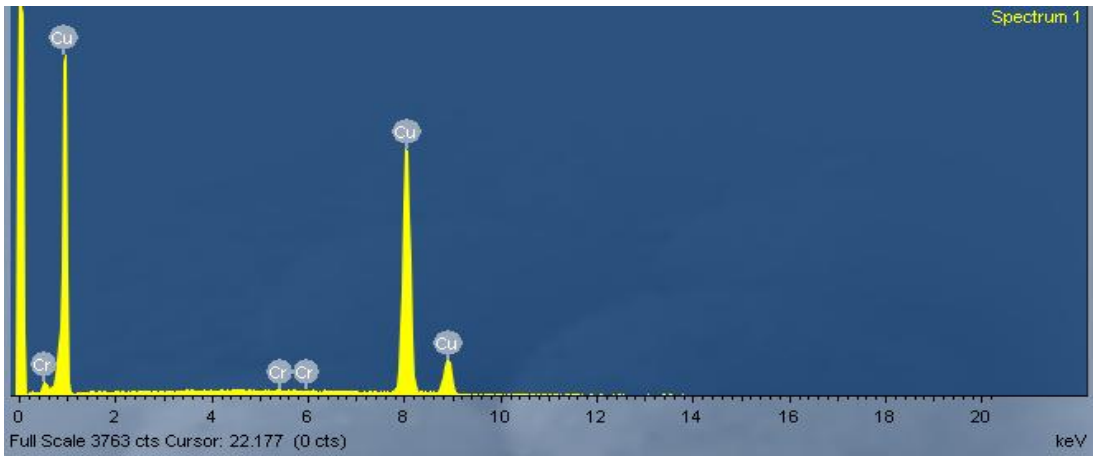

Figure 6.13

Because proper mixing cannot be achieved in 2 h the amount of Chromium is found to be much lower than the initially added amount.

Milling time: 10H

Element	Atomic%
Cr K	0.97
Cu K	99.03
Totals	

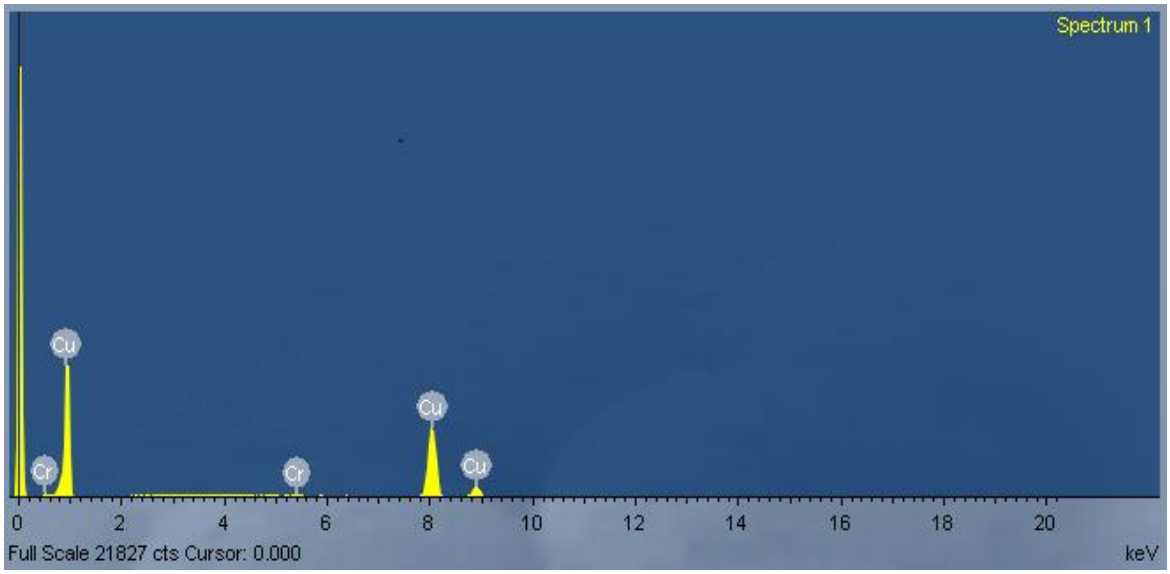

Figure 6.14

With increase in milling time there is increased homogeneity as a result of which the amount of Chromium detected is closer to the initial amount of Chromium in the specimen.

Milling time: 50 h

Element	Atomic%
Cr K	3.62
Cu K	96.38
Totals	

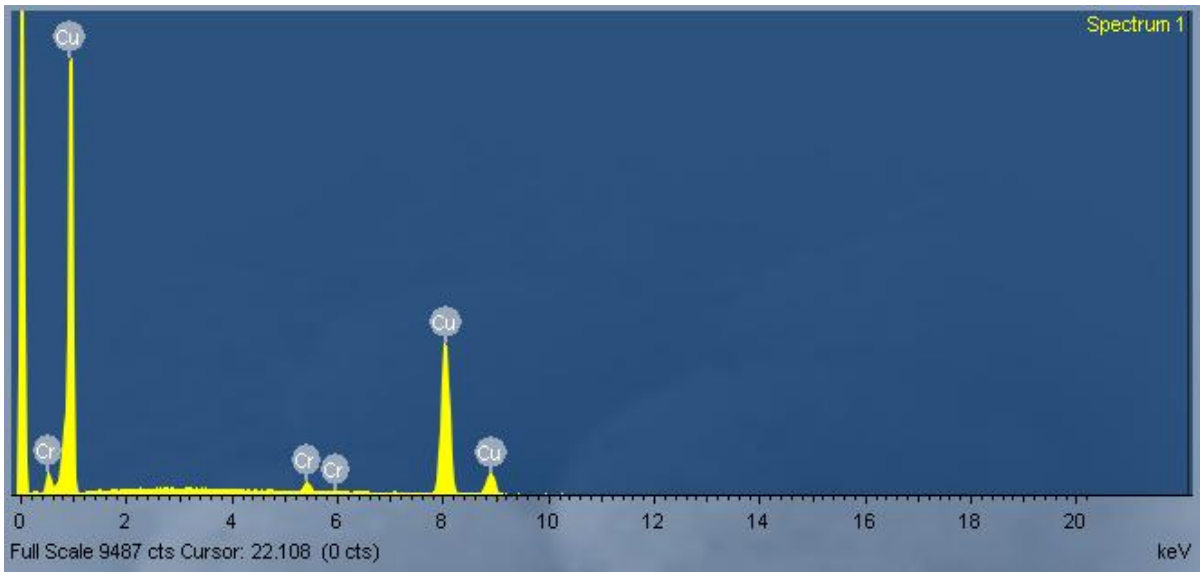

Figure 6.15

The amount of Chromium in this specimen exceeds the initial amount. This may be because of the fact that EDAX is done on a random location. Non homogeneity still persists after 50 h of milling and the region selected for sampling may contain a higher amount of Chromium.

Theoretically ball milling should ensure a homogenous composition even milling time is less but as can be seen from the above observations some amount of inhomogeneity exists even after the samples are milled for as long as fifty hours.

Vickers' microhardness test results:

The results of the Vickers microhardness test are shown in the table below.

Composition	Specimen used	Sintered density (%)	Hv	Avg. Hardness
$Cu_{96}Cr_4$	Specimen 1	81	149.6	146.3
			145.3	
			144.1	
			147.5	
			145.1	
	Specimen 2	83.2	145.1	144.6
			143.5	
			145.3	
			146.4	
			142.9	
$Cu_{95}Cr_5$	Specimen 1	83.7	168.7	167.5
			167.9	
			166	
			168.6	
			166.4	
	Specimen 2	81.5	153.8	153.0
			154.7	
			150.7	
			151.5	
			154.6	

Copper shows a Vickers microhardness value of around 49Hv. On mechanical alloying with Chromium in small amounts as used in preparing the test samples the microhardness value shows a drastic increase. Again the microhardness value increases with increase in Chromium percentage.

SEM Analysis of sintered pellets:

SEM images of both alloy 1 and alloy 2 were taken.

Due to sintering a smooth surface is observed along with some amount of porosity. The presence of pores is also reflected in the density measurement where the density has been found to be between 80-85 %.

Composition 1:

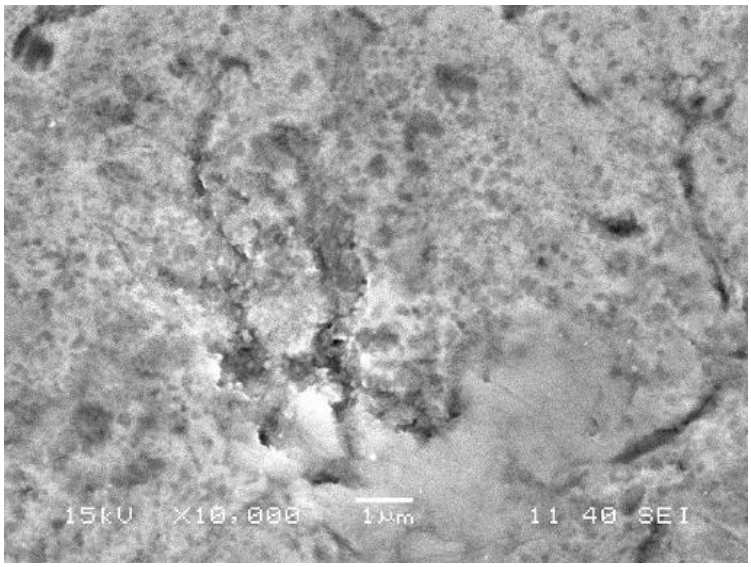

Figure 6.16

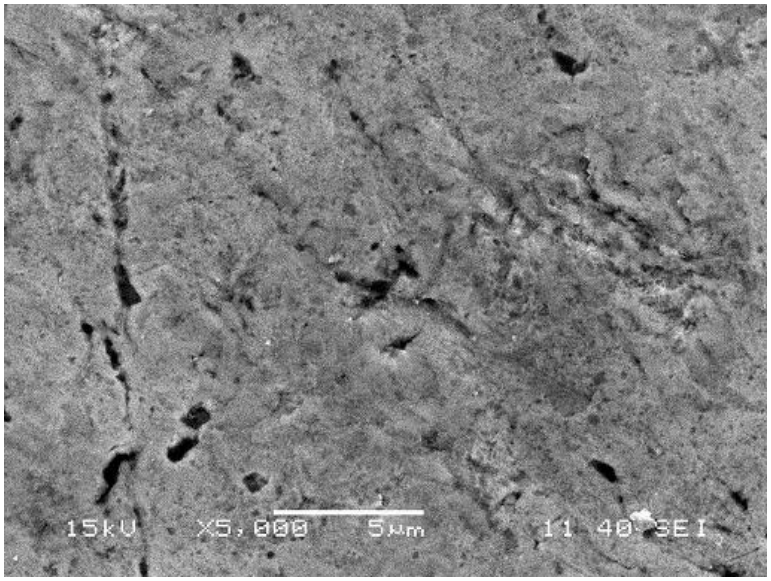

Figure 6.17

Fig. 6.16 Magnification 10000X. Fig. 6.17 Magnification 5000X.

Composition 2:

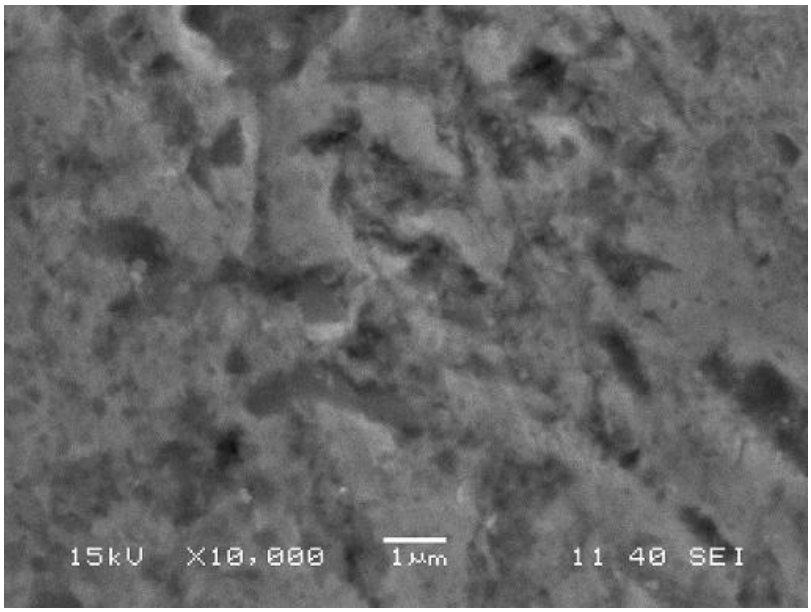

Figure 6.18

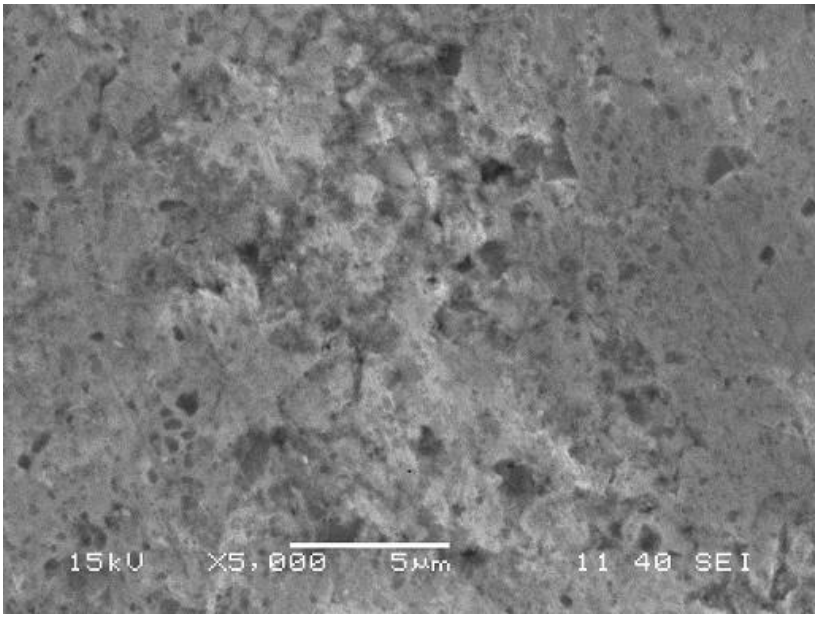

Figure 6.19

Fig. 6.18 Magnification 10000X. Fig. 6.19 Magnification 5000X.

X-ray diffraction:

X-ray diffraction of the compacted and sintered samples was carried out by changing θ from 20° to 100° at 2° per min.

Phase analysis:

Sample 1:

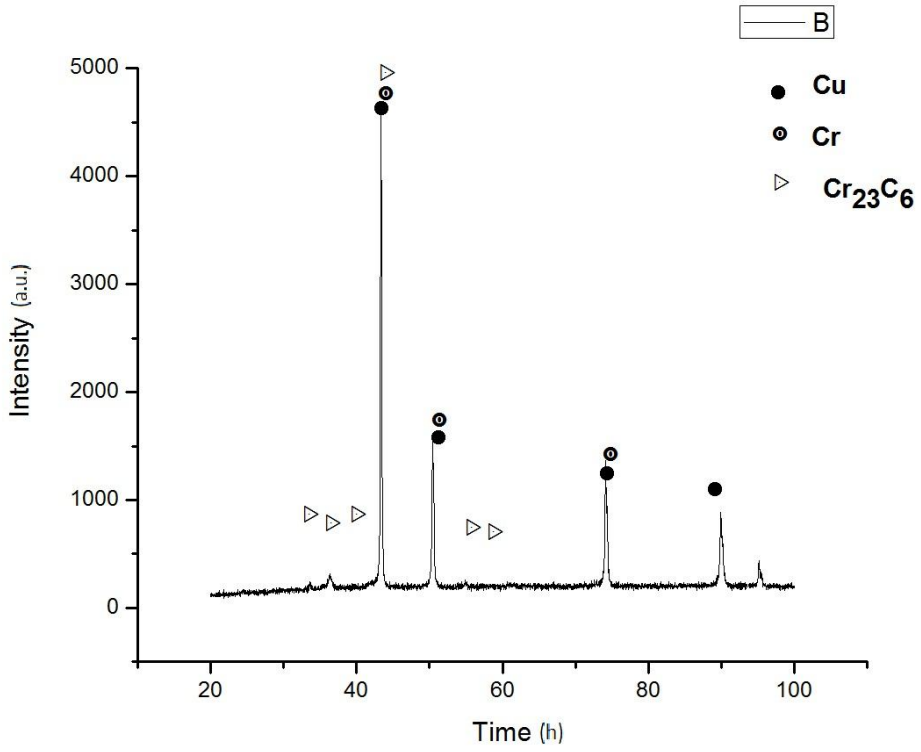

Figure 6.20

The plot shows the presence of various phases along with their relative intensities in the pellet made from sample 1.

Sample 2:

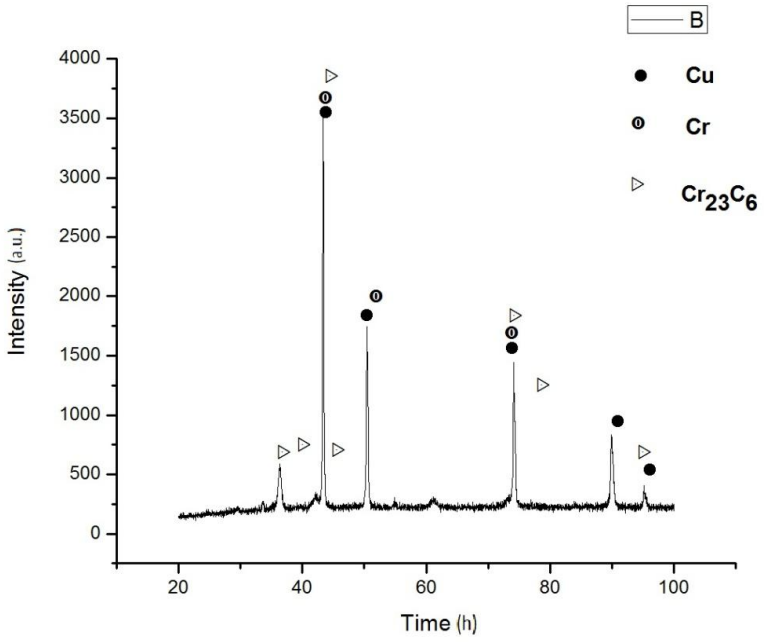

Figure 6.21

The plot shows the presence of various phases along with their relative intensities in the pellet made from sample 2.

The table below shows the variation of Crystallite size and Lattice strain in the pellets made from composition 1 and composition 2.

Parameter	Crystallite Size (nm)	Lattice strain (%)
Sample 1	122.10	0.217
Sample 2	96.06	0.279

It has been observed that crystallite size for specimen 1 is smaller then specimen 2. Similarly the lattice strain for specimen 1 is more then specimen 2. This is due to the more percentage of chromium in specimen 2 then in specimen 1.

Conclusions:

- The XRD study of the prepared samples shows there is a possibility of introduction of compound phases of Cu and Cr due to milling.
- It also shows there is a decrease in crystallite size and increase in lattice microstrain (%) of the prepared nanostructures. The lattice microstrain (%) first increases rapidly and then very slowly with increasing milling time. The lattice microstrain (%) increases because of the plastic and mechanical deformation. The size of the lattice first decreases rapidly and then after a certain time becomes almost constant.
- The SEM analysis shows that there is a definite decrease in the size of the particles formed with increase in milling time.
- The homogeneity of the nanocomposite increases with increase in milling time.
- The compaction was done using uniaxial hydraulic press. The density was found to be between 80-85% after sintering.
- There is a drastic increase in the value of hardness from that of the value of pure Copper with small additions of Chromium. Again the hardness of nanocomposite increases with increase in the amount of Chromium.

Scope for further work:

- Copper nanomaterials find a major use as electrical conductors. Tests should be done for measuring conductivity variations with the amount of chromium addition. Other mechanical properties like wear resistance can also be measured.
- Due to the presence of porosity there is further scope for improvement in mechanical properties if compaction can be done using advanced techniques like hot isostatic pressing.

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